ROTATION-VIBRATION SPECTRUM OF H_2 IN NANOCAGES

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Abstract

We discuss the energy level structure for an H_2 molecule confined within either interstitial cavities in C_{60} or nanotubes. A free H_2 molecule has energy levels $E_J = BJ(J+1)$ of degeneracy $(2J+1)$, where the rotation quantum of energy, B, is of order 7 meV. In the confined geometry considered here, the orientationally dependent part of the potential is small enough that J remains a good quantum number, at least as long as the translational kinetic energy is below, say, 50 meV. For $J=0$ molecules (para-H_2) one has the energy level spectrum of a sphere in the confined geometry mentioned above. For ortho-H_2 (for which $J=1$) we have the simplest model of rotation-translation coupling. In this case, instead of a scalar wave function $\psi(\mathbf{r})$, one has to determine a three component wave function

$$F(\mathbf{r},\omega) = \sum_{M=-1}^{1} \psi_M(\mathbf{r}) Y_1^M(\theta,\phi) \ , \tag{1}$$

where $\omega \equiv (\theta,\phi)$ and $Y_1^M(\theta,\phi)$ is a spherical harmonic. When we neglect the coupling between rotations and translations, the eigenfunction $F(\mathbf{r},\omega)$ is a product of a function of position and a function of molecular orientation, where the orientational function is a linear combination of spherical harmonics $Y_J^M(\theta,\phi)$. In the presence of a realistic potential there inevitably is coupling between these $2J+1$ product functions and one now has a nonseparable quantum wave function of the form written in Eq. (1).

For octahedral interstital cavities in C_{60}, the symmetry of these rotation-vibration wave functions is easily discussed in a basis in which phonons have angular momentum 1 $(x+iy)$, 0 (z), or -1 $(x-iy)$. Then the problem reduces to the familiar problem of addition of angular momentum in a cubic field. To illustrate the flavor of our results we show cartoons of various simple vibration-rotation wave functions and compare these to what one expects for classical dynamics. Results from a numerical solutions to the rotation-translation Hamiltonian and a brief comparison to neutron time-of-flight data is presented.

The same type of treatment also applies to H_2 in carbon nanotubes. Because the H_2 molecule is bound to the wall of the nanotube, there are two regimes: When the nanotube radius is small (as for a 5,5 tube), the potential is essentially nearly parabolic and the H_2 molecule oscillates about the center of the tube mcuh as it does in C_{60}. When the nanotube radius is larger (i. e. for 10, 10 tubes), one has a Mexican hat poential in which in the ground state the H_2 molecule lives predominantly in a cylindrical shell rather than being at the axis of the tube. In this case one has wavefunctions of the form of Eq. (1) except that $Y_1^M(\theta,\phi)$ is here replaced by $e^{iM\phi}$. In both regimes, we have developed a simple toy model which enables us to understand the nature of the spectrum of roation-vibration states.

References

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